

Inner Surface Modification of Steel Tubes using a Duplex Technique of Hot-dipping and Plasma Electrolytic Oxidation¹

Wei-Chao Gu, Guo-Hua Lv, Huan Chen, Si-Ze Yang*, Fang Qin**

**Beijing National Laboratory for Condensed Matter Physics, Institute of Physics,
Chinese Academy of Sciences, Beijing, 100080, P.R.China*

Phone: +86-10-8264-9458; Fax: +86-10-8264-9531, E-mail: yangsz@aphy.iphy.ac.cn

***Anshan Yin-ma Hot-dipping Aluminium-plating Co. Ltd., Anshan, 114001, P.R.China*

Abstract – A new method for inner surface modification of steel tubes, named a combined technique of hot-dipping and plasma electrolytic oxidation (PEO), was proposed and demonstrated in this paper. The element distribution, phase composition, and morphology of the aluminide layer and the ceramic coatings were characterized by SEM/EDX and XRD. The hardness and corrosion resistance of the ceramic coatings were also tested. The results show that, after hot-dip treatment, the coating layers consist of two layers, where Al, $\text{Fe}_x\text{Al}_{(1-x)}$ were detected from external topcoat to the aluminide/steel substrate. Then after PEO process, uniform Al_2O_3 ceramic coatings have been deposited on inner surface of steel tubes. The ceramic coatings are mainly composed of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ phase. The compound coatings show high hardness and favorable corrosion resistance property. The investigations indicate that the combination of hot-dipping and plasma electrolytic oxidation proves a promising technique for inner surface modification of steel tubes for protective purposes.

1. Introduction

Modification treatment for the surface of materials using various surface techniques has become one of the most active fields and an important section for increase of work-piece life and economy efficiency. Steel is easy to work, especially for its high tensile strength and excellent plastic and tough characteristics. However, the wear and corrosion resistance of steel are much lower than those of ceramic materials. A number of deposition techniques such as arc-discharge plasma, gas-flame spray, vacuum deposition methods and high temperature glass enameling have been investigated to produce ceramic coatings on steel. But these techniques require a high substrate temperature to provide adequate coating adhesion at high contact loads. Furthermore, most of these techniques are not fit to applications for complicated surface of work-pieces, such as long steel tubes.

Plasma electrolytic oxidation (PEO) is a novel technique that can be used to form metallurgically bonded ceramics on some non-ferrous metals, such

as Ti, Al, Mg, Nb, etc., and their alloys [1–6]. Earlier research showed that the coatings offered attractive combination of wear resistance, corrosion resistance and mechanical strength [7–9]. Components of irregular shape can also be processed by PEO conveniently to form uniform ceramic protective coatings on their surface. Actually, axially uniform coatings on the inner surface of aluminum tubes can be obtained recurring to a central accessorial cathode in our previous study. But this promising technique cannot be used to modify the surface properties of steel, which is the most widely used material in engineering.

A new method has been attempted to prepare metallurgically bonded ceramic coatings on inner surface of steel tubes in our laboratory for protection purpose. In the combined process, aluminum coatings on steels were firstly prepared by the hot-dip process, which is an effective and inexpensive modification method, and then metallurgically bonded ceramic coatings were obtained on aluminum coatings by PEO. To the best of our knowledge, this method for inner surface modification of steel tubes has never been reported.

2. Experimental procedure

Materials of 0.20 wt. %C steel tubes with inner diameter of 50 mm and length of 500 mm were used as substrate. Aluminum alloys (the nominal composition in weight percent: Cu 0.01 %, Fe 0.16 %, Si 0.16 %, Zn 0.04 %, Ti 0.02 % and Al balance) were used as the hot-dipping material. After polishing machining the samples were degreased in acetone bath and finally cleaned in ethanol bath, and dried in air before hot-dip aluminizing. The aluminum alloys were melted in a crucible and maintained at 700 °C. The hot-dipped tubes were cleaned by a mixed aqueous solution of nitric acid, phosphoric acid, and water in a 1:1:1 volume ratio at 25 °C. After hot-dip aluminizing, metallographical examination was carried out to study the element distribution, phase composition, and cross-section morphology.

¹ The work was supported by the National High Technology Research and Development Program of China (863 Program) under Grant No. 2002A331020.

PEO was carried out with a built in-house 20 kW PEO system. The electrolysis environment was an aqueous electrolyte containing sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3) and sodium hexametaphosphate ($(\text{NaPO}_3)_6$) of the chemical grade solution at concentration of 0.025 M, 0.066 M and 0.008 M, respectively. Throughout the entire range of experimentation, the temperature of the electrolyte maintained constantly at 40 ± 2 °C using a heat exchanger. Designedly, a central accessorial cathode was placed inside the tube to eliminate the effect of electric field shield.

After the combined processes, the tube was cut into small blocks. The phase constitutions in the compound layers of all specimens were investigated by means of metallographical examination, scanning electron microscopy (SEM) with energy-dispersive X-ray facility analysis (EDX) and X-ray diffraction (XRD) using Cu-K α radiation. In addition, the microhardness profile across the coatings depth was measured using a Nano-Indenter XP of MTS. The potentiodynamic polarization curves were performed to evaluate the corrosion protective property.

3. Results and discussion

A typical cross-section morphology of an as-coated steel after hot-dipping is shown in Fig. 1, *a*, where three layers are presented: topcoat aluminum, intermetallics and the steel substrate. Typically, the thickness of the coating layers was about 300 μm and the coating layers showed good adhesion to the steel substrate. Fig. 1, *b* shows the microstructure of the top Al-rich layer, which shows a compact structure, and no obvious apertures and cracks can be seen in it.

The interface between the Fe substrate and the inter metallic layer appears tongue-like morphology [shown in Fig. 1, *c*]. The tongue-like morphology suggests diffusion of iron and Al elements in the hot-dip process. The morphology also implies that metallurgical reaction that takes place at the surface of the steel substrate as it enters the liquid alloy leads to formation of intermetallic compounds [10].

The characteristic EDX spectra corresponding to the line (A–B) in the micrograph in Fig. 2, *a* is shown in Fig. 2, *b*. As can be seen, qualitatively, the chemical composition of the topcoat layer is mainly aluminum, and the individual intermetallic compound particles are composed of Fe and Al. The relative concentration of the elements found on the coated layer and their distribution from the coated layer to the interior is given in Fig. 2, *b*. As can be seen, the Fe content is about two times lower than Al in the intermetallic region.

In order to find out the phase composition of the hot-dipping coating, specimens were polished to different depths. XRD analysis results show that the phase compositions of the hot-dipping coating are mainly of Al outside and $\text{Fe}_x\text{Al}_{(1-x)}$ (mainly Fe_2Al_5 and a little Fe_4Al_3) inside from the external topcoat to the aluminide/steel substrate, which is roughly consonant with the above EDX analysis result. It is clear

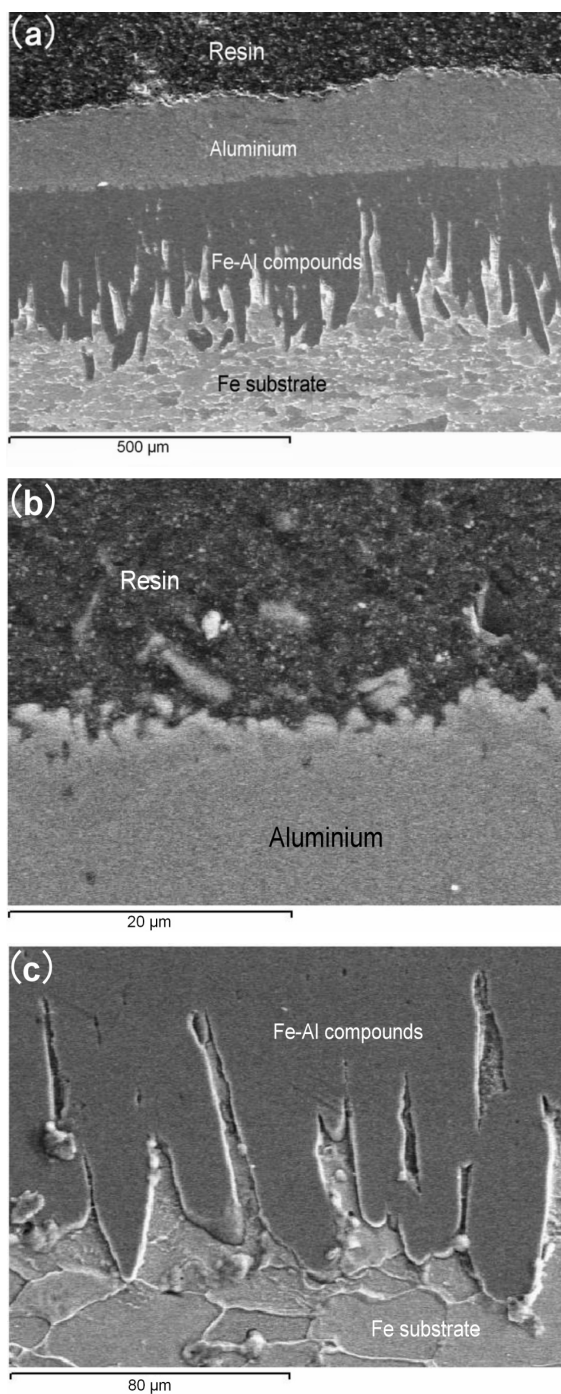


Fig. 1. Cross-section micrographs of the specimen after hot-dipping treatment: (a) panorama of the coating; (b) topcoat aluminium; (c) Fe-Al intermetallics between aluminium coating and steel substrate

that the compounds of Fe and Al appear near the interface but pure aluminium remains at the outer layer. This kind of composition and structure distribution is very suitable for the subsequent PEO processes.

Fig. 3 shows the SEM fractograph of the PEO ceramic coating. The PEO ceramic coating does not have distinct loose superficial layer and dense inner layer, which is different from the coating structure prepared on Al alloy [4]. Microcracks appear in the

PEO coating, which could be initiated by the thermal stress attributed to the rapid solidification of the alumina melted in the discharge channel. In the discharge channel, the instantaneous temperature can reach 7000 K [11]. The melted alumina has an intimate contact with the cool electrolyte and the cooling velocity even reaches 10^8 K/s [12], so the appearance of the cracks in the structure of the PEO coatings is inevitable, just as the microcracks appear on the surface of the PEO ceramic coatings [4]. Even so, no palpable apertures were observed at the interface between the substrate and the coatings according to the SEM investigation. It is clear that the interface of aluminium/ceramic coatings are well metallurgically bonded, which indicates that the PEO coatings can be a good candidate as protective coatings.

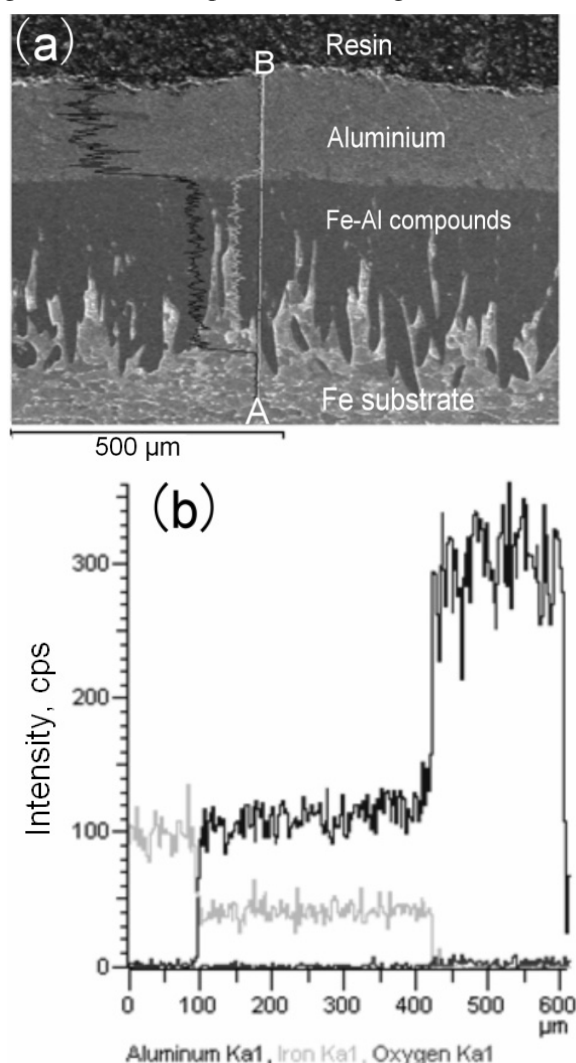


Fig. 2. EDX analysis of the hot-dipping coating

The X-ray diffraction pattern of the ceramic coatings shows that the PEO coatings mainly consist of α - Al_2O_3 and γ - Al_2O_3 . Finally, there appears to be a significant amount of textured aluminium, and this is probably due to X-ray penetration through to the aluminium substrate. The result is consonant with

other researchers' reports on PEO coatings fabricated on aluminium alloys [3, 8, 13, 14].

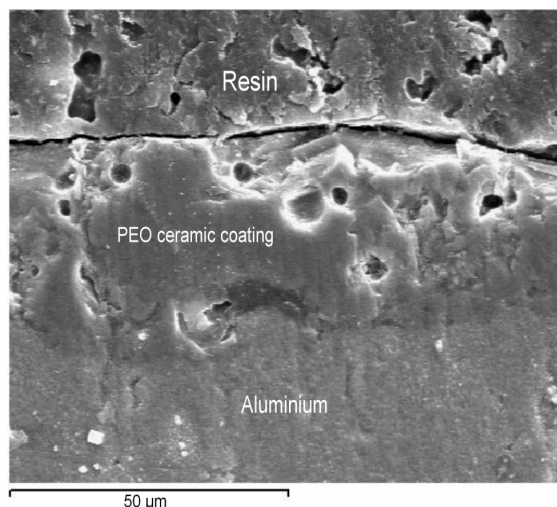


Fig. 3. SEM micrograph of the cross-section features of the ceramic coating

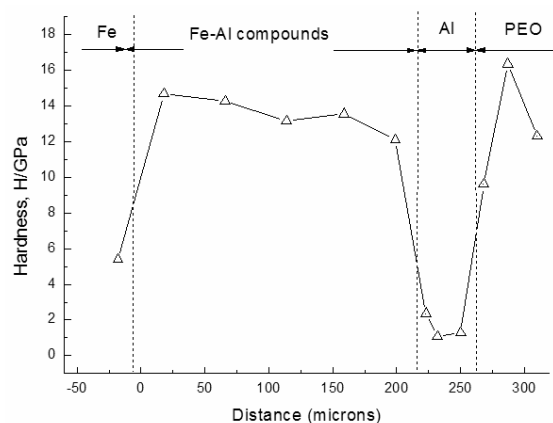


Fig. 4. Microhardness profile of coatings on 0.2 wt % Fe substrate

Fig. 4 displays microhardness profile of coatings on 0.2 wt % Fe substrate. From the outer layer to the interior of the coating, the microhardness gradually changes. Its maximum value is about 16 GPa at the PEO coating part. It is much higher than hardness of the 0.2 wt % Fe substrate. The middle hot-dip aluminium coating has the lowest hardness, which may be disadvantageous to the mechanical properties of the compound coatings. However, the aluminium coating can be turned into ceramic by adjusting the PEO processing time.

The electrochemical measurements were performed using a Princeton Applied Research (PAR) EG&G potentiostat/galvanostat model 283 with model 270 corrosion software. All electrochemical measurements were conducted using a conventional three electrodes electrochemical cell with the coated samples as the working electrode, a platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference. The working electrode

was embedded with epoxy resin to leave 1 cm² surface to be accessed by the test solution.

The typical potentiodynamic polarization curves of samples coated with PEO ceramic coating as well as the substrate untreated are displayed in Fig. 5. The corrosion resistance of different layers across the coatings depth were also tested with samples polished to different depths. The corrosion potentials (E_{corr}), corrosion current densities (I_{corr}) and anodic/cathodic tafel slopes (β_A and β_C) were calculated from these tests. Then, based on the approximate linear polarization at the corrosion potential (E_{corr}), polarization resistance (R_p) values were determined by the relationship between them [15].

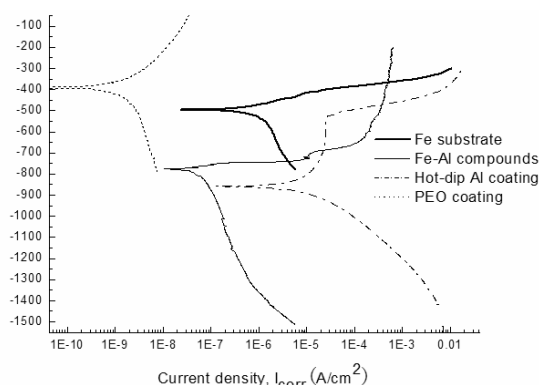


Fig. 5. Polarization curves of the coatings in 3.5 % NaCl aqueous solution

Table 1. Electrochemical parameters related to potentiodynamic polarization curves

Samples	Fe	Fe-Al	PEO
E_{corr} (mV)	495.5	783.9	389.9
I_{corr} ($\times 10^{-9}$ A/cm ²)	1150	56.05	1.87
β_A (mV/decade)	86.33	44.16	270.83
β_C (mV/decade)	307.52	504.93	829.15
R_p ($\times 10^4$ Ω /cm ²)	2.68	33.5	4540

A summary of the electrochemical corrosion parameters derived from the polarization curves are also listed in Table 1. Apparently, the curve of the 0.2 wt % Fe substrate with ceramic coating was shifted 104 mV to the positive direction relative to the curve of the uncoated samples, which indicates that the corrosion protection property of the coated samples is better than that of the uncoated one. Regarding the corrosion rate, the results show that the corrosion current density (I_{corr}) and the polarization resistance (R_p) of the samples coated with ceramic coating is at least three orders of magnitude lower and three orders of magnitude higher than those of the uncoated samples. Furthermore, the Fe-Al compounds also exhibit high corrosion resistance compared with the Fe substrate. The compound structure indicates that the coatings provide two-tier protection for the Fe substrate. In other words, compound coatings formed on steel surface by the combined method provide effective corrosion protective property in solutions containing Cl⁻ ions.

4. Conclusions

A combined process of hot-dipping and plasma electrolytic oxidation was applied for deposition of ceramic coatings on inner surface of steel tubes for protective purpose. The phase compositions of the compound coatings inside are ceramic coating, aluminum and Fe_xAl_(1-x) (mainly Fe₂Al₅ and a little Fe₄Al₃) from the external topcoat to the steel substrate and every two layers are metallurgically bonded with each other. The ceramic coatings as the external topcoat are mainly composed of α -Al₂O₃ and β -Al₂O₃ phase. Compound coatings exhibit high hardness and excellent corrosion resistance. All these characteristics indicate a feasible and effective method for forming protective coatings on inner surface of steel tubes.

Acknowledgements

Financial support for this work were provided by the National High Technology Research and Development Program of China (863 Program) under Grant No. 2002A331020.

References

- [1] T.B. Van, S.D. Brown, G.P. Wirtz. Am. Ceram. Soc. Bull. 56, 563 (1977).
- [2] A.L. Yerokhin, A. Leyland, A. Matthews. Appl. Surf. Sci. 200, 172 (2002).
- [3] Yang Guangliang, Lü Xianyi, Bai Yizhen, Cui Haifeng, Jin Zengsun. J. Alloys Compd. 345, 196 (2002).
- [4] Tongbo Wei, Fengyuan Yan, Jun Tian. J. Alloys Compd. 389, 69 (2005).
- [5] P.A. Dearnley, J. Gummersbach, H. Weiss, A.A. Ogwu, T.J. Davies. Wear. 225–229, 127 (1999).
- [6] G.P. Wirtz, S.D. Brown, W.M. Kriven, Mater. Manuf. Process. 6, 87 (1991).
- [7] Wenbin Xue, Chao Wang, Zhiwei Deng, Yongchun Lai, Tonghe Zhang. J. Phys.: Condens. Matter. 14, 10947 (2002).
- [8] J.A. Curran, T.W. Clyne. Surf. Coat. Technol. 199, 168 (2005).
- [9] Yaming Wang, Tingquan Lei, Bailing Jiang, Lixin Guo. Appl. Sur. Sci. 233, 258 (2004).
- [10] F. García, A. Salinas, E. Nava. Mater. Lett. 60, 775 (2006).
- [11] M.D. Klapkiv. Mater. Sci. 314, 94 (1995).
- [12] A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews. Surf. Coat. Technol. 122, 77 (1999).
- [13] P.I. Butyagin, Ye.V. Khokhryakov, A.I. Mamaev. Mater. Lett. 57, 1748 (2003).
- [14] Xue Wenbin, Deng Zhiwei, Lai Yongchun, Chen Ruyi. J. Am. Ceram. Soc. 81, 1365 (1998).
- [15] X. Nie, E.I. Meletis, J.C. Jiang, A. Leyland, A.L. Yerokhin and A. Matthews, Surf. Coat. Technol. 149, 245 (2002).